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Stöger et al.

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[54] **APPARATUS AND METHOD FOR THE ELECTRODEPOSITING OF ALUMINUM**

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[51] **Int. Cl.**[2] **C25D 5/00;** C25D 5/04

[52] **U.S. Cl.** ..... **204/14 N;** 204/237; 204/213

[58] **Field of Search** ..... 204/14 N, 275, 213, 204/237

[56] **References Cited**

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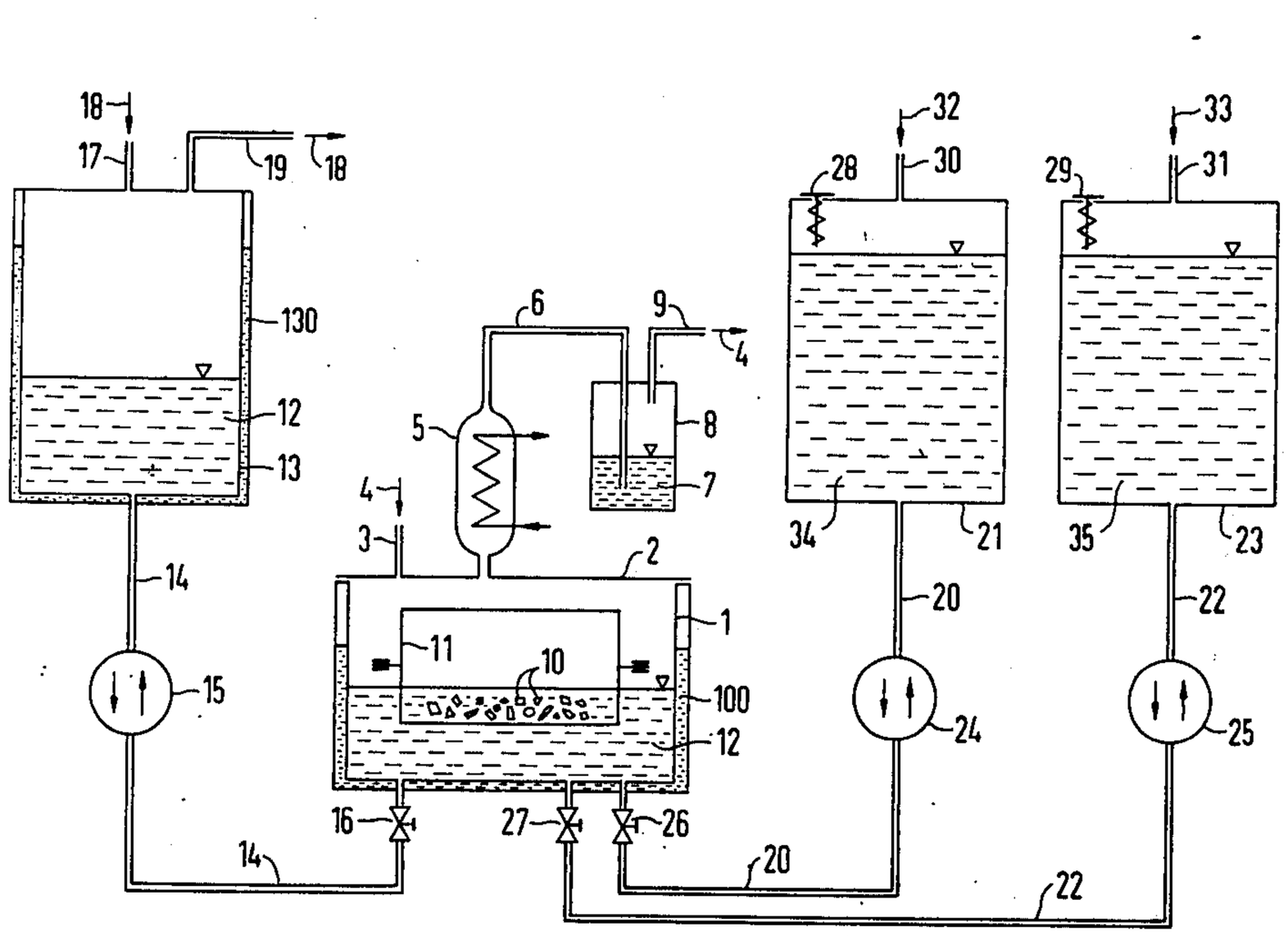
[57] **ABSTRACT**

Apparatus for electrodepositing aluminum from aprotic, oxygen-free and water-free organo-aluminum electrolytes in which a heatable treatment tank is closed off in an airtight manner and contains a rotatable electroplating drum with a first heatable tank for storing an aprotic oxygen-free and water-free organo-aluminum electrolyte and a second tank for storing a rinsing liquid connected to the treatment tank.

10 Claims, 3 Drawing Figures



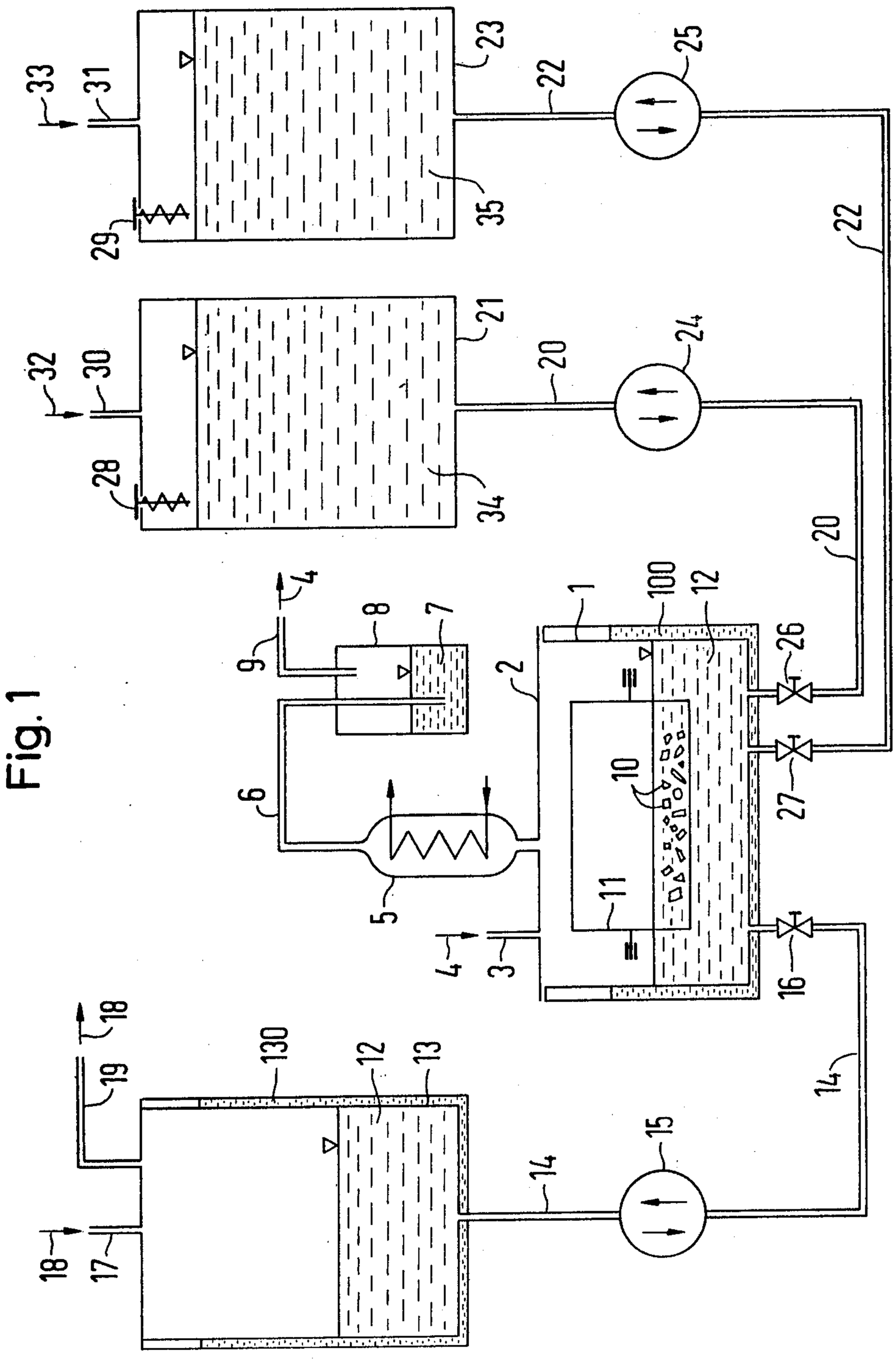

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Fig. 1

Fig. 2

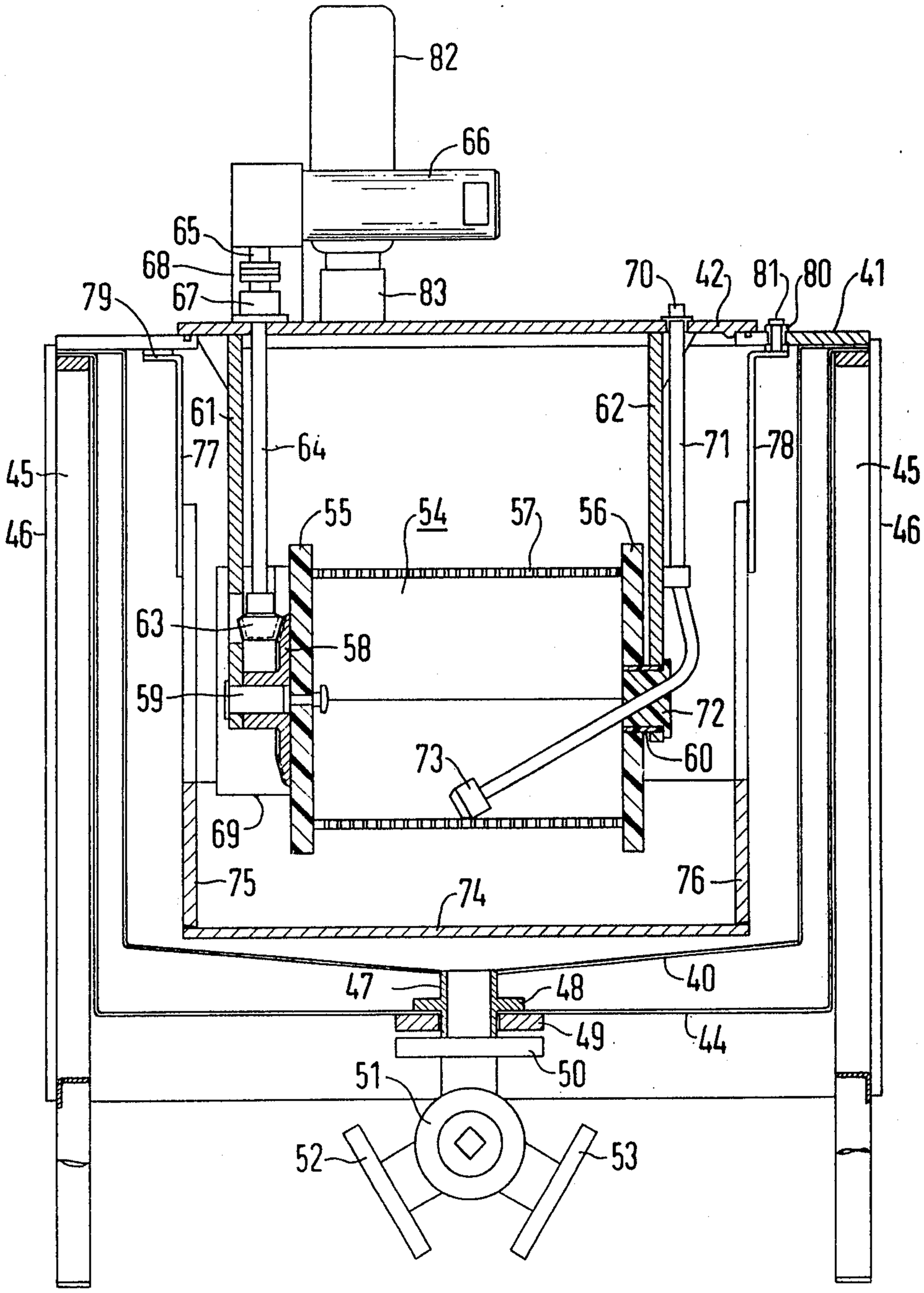
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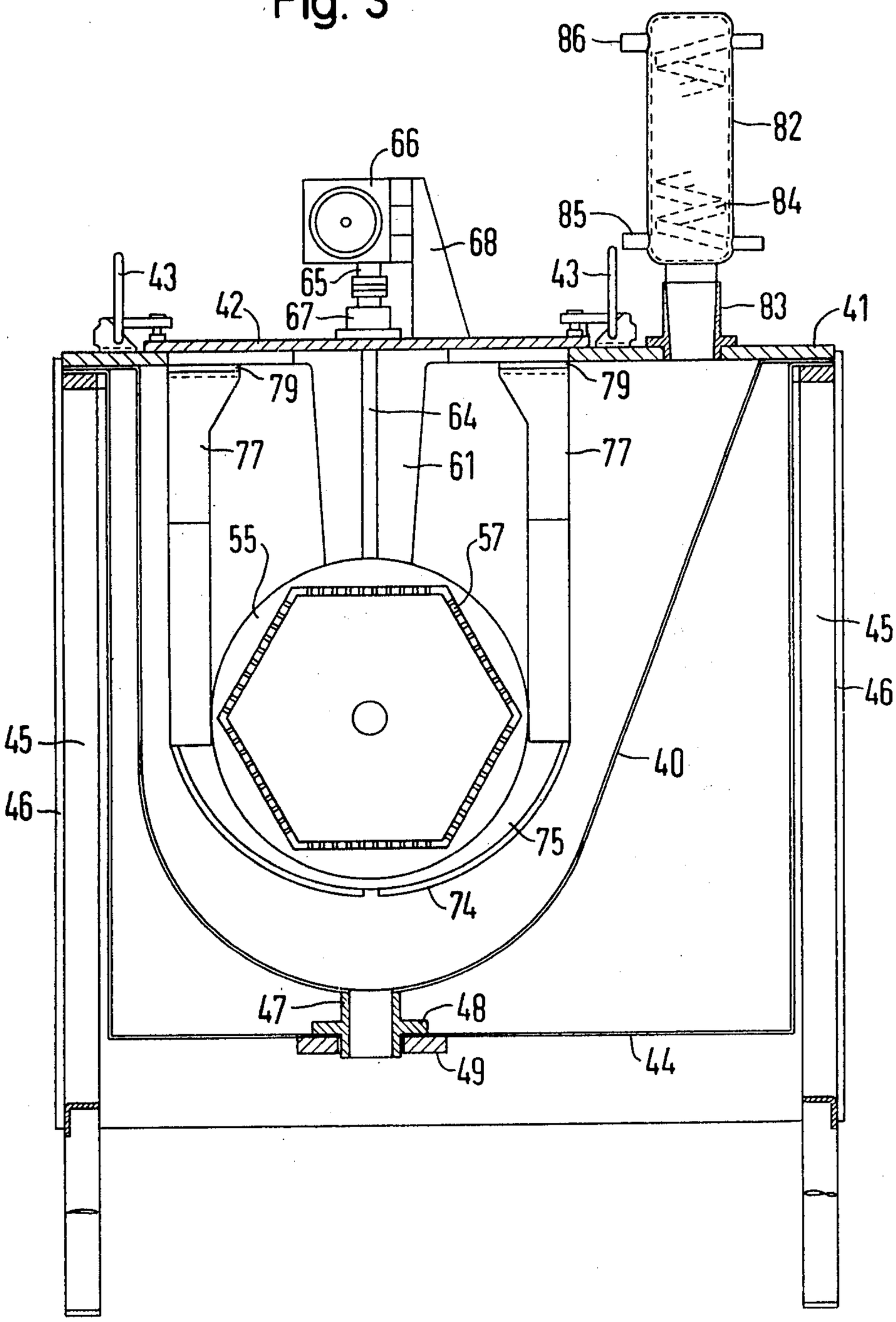
Fig. 3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APPARATUS AND METHOD FOR THE ELECTRODEPOSITING OF ALUMINUM

BACKGROUND OF THE INVENTION

The invention relates to apparatus for electrodepositing aluminum from aprotic, oxygen-free and water-free organo-aluminum electrolytes in general and more particularly to improved apparatus of this nature.

Aluminum electrodeposited from aprotic, oxygen-free and water-free organo-aluminum electrolytes has been found highly suitable for many engineering purposes because of its ductility, freedom from pores, corrosion resistance and ability to be anodized. Such electrolytes, which are known, for instance, from U.S. Pat. Nos. 3,448,127 and 3,418,216 and British patent specification No. 1,001,482, are prepared and stored under oxygen-free and water-free conditions. Since the access of air causes a considerable reduction of the conductivity and the life of these electrolytes because the electrolyte reacts with the oxygen and the moisture of the air, the electrolyte bath must be protected from contact with air as thoroughly as possible. Attemptes to carry out the electrodeposition of aluminum in known electroplating apparatus and to accomplish the exclusion of air by covering the electrolytic bath with protective liquids such as paraffin oil or inert gases such as nitrogen, however, have not led to satisfactory results. Such coverings do not provide a reliable protection of the electrolytic bath, since they are repeatedly torn open when the articles to be electroplated are inserted and removed as well as when the electrolyte and/or the articles move. Such operations thus permit air to come into contact with the electrolyte. In addition, the use of an inert gas for protection is not possible since inert gases mix very easily with the ambient air, so that a closed inert gas layer would not provide reliable air exclusion either.

SUMMARY OF THE INVENTION

It is therefore an object of the invention to provide an apparatus for electrodepositing aluminum, in which the electrolyte can be kept under oxygen-free and water-free conditions.

According to the present invention, an apparatus of this type is provided which includes: a heatable treatment tank which is sealed airtight and to which an inert gas can be admitted; a rotatable electroplating drum arranged inside the treatment tank; a first tank, connected to the treatment tank for storing the electrolyte and a second tank, connected to the treatment tank, for storing a rinsing liquid.

With the apparatus according to the present invention, the electrolyte can be reliably protected from contact with the air at any time in the electroplating process. For this purpose, the treatment tank is first filled with dry inert gas and then with the rinsing liquid stored in the second tank, so that the air present is completely displaced. After replacing the rinsing liquid back into the second tank, only inert gas is still present in the treatment tank. Now the electrolyte stored in the first tank can be filled into the treatment tank without contamination. After the aluminum is deposited, the electrolyte is again stored in the first tank and the treatment tank is then charged with rinsing liquid for rinsing the articles to be plated, and the articles to be plated are rinsed clear of adhering electrolyte while the plating drum rotates.

The electrolyte is stored in a heatable first tank at the operating temperature required for the aluminizing, so that it need not first be heated before it is filled into the treatment tank.

The treatment tank is preferably connected to a third tank, the third tank being provided for storing a second rinsing liquid. By means of the second rinsing liquid, the plated articles are freed of electrolyte residue and hydrolysis products in the treatment tank. By use of the second rinsing liquid, the content of electrolyte and hydrolysis products in the first rinsing liquid is substantially reduced, so that a replacement of the first rinsing liquid is necessary now only after fairly long intervals of time.

Advantageously, the treatment tank is connected to the other tanks via feed pumps. The feed pumps make is possible to displace the electrolyte and the rinsing liquid rapidly and therefore, to accelerate the electroplating cycle.

In one embodiment of the apparatus according to the invention, a cover, at which the supports of the plating drum are fastened, is provided for closing off the treatment tank. For inserting and removing the articles to be plated, the cover need be lifted only far enough so that the plating drum is accessible. It is therefore no longer necessary to remove the plating drum separately.

Preferably, a reflux cooler is provided in the upper portion of the treatment tank. In the reflux cooler, solvent vapors rising from the electrolyte as well as vapors of the rinsing liquid are condensed and returned to the treatment tank. The losses of the several treatment liquids can thereby be kept extremely low.

It is advantageous to connect to the treatment tank a relief line, the end of which is immersed in an inert sealing liquid. The relief line is provided for the pressure relief of the treatment tank and for discharging the inert gas displaced by the different treatment liquids. The admission of air to the treatment tank is reliably prevented by the sealing liquid. The relief line immersed in a sealing liquid is distinguished by its simplicity over other possibilities for achieving pressure relief and equalizing volume variations of the inert gas, such as by connecting a gas tank filled with inert gas.

In accordance with further features of the present invention, the described apparatus is operated so that first, a water-free aprotic rinsing liquid is placed in the treatment tank and is subsequently relocated into the second tank, and that then the electrolyte is admitted into the treatment tank and returned to the first tank after the electrodeposition is finished. With this procedure, the air which penetrates into the treatment tank when the articles to be plated are placed in it is completely replaced by the rinsing liquid and the inert gas.

The plating drum with the articles to be plated is preferably immersed into the treament tank filled with the rinsing liquid. The articles to be plated, which are bare and free of cover layers after a suitable surface treatment and are wetted by a protective liquid, can be immersed in the rinsing liquid immediately after they are filled into the plating drum, before the rinsing liquid evaporates.

The treatment tank is advantageously filled, after the electrolyte is relocated, with a second, water-free, inert aprotic rinsing liquid. In this manner, the plating drum and the articles to be plated can easily be freed of residual electrolyte and hydrolysis products.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic presentation of an apparatus for the electrodeposition of aluminum.

FIGS. **2** and **3** are a longitudinal view and a cross section, respectively, of an apparatus in accordance with the present invention without the required storage tanks.

DETAILED DESCRIPTION OF THE INVENTION

FIG. **1** shows a treatment tank **1**, which is closed off by a cover **2** and to which inert gas **4** can be admitted via a feed line **3**. The excess inert gas is conducted through an opening in the cover **2** into a reflux cooler **5**, in which vapors that might be carried along are condensed, so that the condensate flows back into the treatment tank **1**. From the reflux cooler **5**, the excess inert gas **4** is conducted via a line **6** into an inert sealing liquid **7**, such as, for instance, paraffin oil. The sealing liquid **7** is contained in a vessel **8** which is designed like a wash bottle and has an outlet **9** for the protective gas.

Inside the treatment tank **1**, a rotatable plating drum is arranged, which contains the articles **10** to be electroplated and the lower part of which is immersed in an aprotic, oxygen-free and water-free organo-aluminum electrolyte **12**. The treatment tank is surrounded by a heating bath **100** so that the electrolyte **12** can be kept at an operating temperature of 80° to 100° C. The electrolyte **12** is filled in from a closed tank **13** which is surrounded by a heating bath **130** and is connected to the treatment tank **1** via a line **14**. A feed pump **15** and a valve **16** are disposed in the line **14**. Inert gas **18** is admitted to tank **13** via a feed line **17** so that the electrolyte **12** in the tank **13** does not come into contact with air. The outlet **19**, not further detailed, for the protective gas **18** can be run, as in the case of the treatment tank **1**, via a reflux cooler and an inert sealing liquid.

The treatment tank **1** is further connected via a line **20** to a closed tank **21** and via a line **22** to a closed tank **23**. The two lines **20** and **22** contain feed pumps **24** and **25** as well as valves **26** and **27**. The tanks **21** and **23**, which are equipped with overpressure valves **28** and **29** and to which inert gas **32** and **33**, respectively, can be admitted via feed lines **30** and **31**, are provided for storing rinsing liquids **34** and **35**. The two rinsing liquids **34** and **35**, under inert gas pressure, must be oxygen-free and water-free; aromatic hydrocarbons such as toluol and xylol are particularly well suited for this purpose.

The supply of the inert gases **4**, **18**, **32** and **33** may be interconnected; nitrogen, argon, krypton and gaseous hydrocarbons are suitable inert gases.

Feed pumps **15**, **24** and **25** which can be switched, i.e., their directions of pumping can be reversed are preferably employed. However, pairs of pumps, which can be connected at will, with opposite pumping directions may also be used. Similarly, the pumping can be accomplished by acting upon the different liquid levels with the protective gas via an appropriate pressure control.

Before the articles **10** to be plated are placed in the apparatus described, they must be subjected to a pre-treatment for creating bare surfaces, which are free of cover layers. A suitable surface pre-treatment is described, for instance, in U.S. Pat. application Ser. No. 419,233 filed Nov. 27, 1973. The subsequent aluminizing includes the following process steps:

a. the articles **10** to be plated, still wet with a protective liquid from the pre-treatment, are placed in the plating drum **11**;
b. the plating drum **11** is immersed in the treatment tank **1** filled with the rinsing liquid **34** and the cover **2** is thereupon closed;
c. the rinsing liquid **34** is pumped back into the tank **21**;
d. the electrolyte **12** is pumped from the tank **13** into the treatment tank **1** until the desired electrolyte level is reached;
e. the articles **10** to be plated are electroplated with aluminum while the plating drum **11** rotates;
f. the electrolyte **12** is pumped back from the treatment tank **1** into the tank **13**;
g. the rinsing liquid **35** is pumped into the treatment tank **1** and the plated articles **10** are freed of electrolyte residue and hydrolysis products, while the plating drum **11** rotates;
h. the rinsing liquid **35** is pumped back into the tank **23**;
i. the cover **2** is opened and the plated articles **10**, coated with aluminum are removed from the plating drum **11**.

FIGS. **2** and **3** show an apparatus for electrodepositing aluminum, without the corresponding storage tanks, in a longitudinal and a cross section, respectively. The treatment tank **40** of this apparatus is closed by an upper cover plate **41**, into which a cover **42** is fitted. The cover **42** is closed and opened by locking devices **43**, which are fastened on the cover plate **41**. The treatment tank **40** is hung in a heating tank **44** which contains a heating bath, e.g., an oil bath. The heating system, not shown in the drawing, of the heating bath may use, for instance, heater cartridges or a connection to a circulating heating system. The treatment tank **40** and the heating tank **41** are hung together in a frame **45** which is mounted on four legs and has an outer enclosure **46**. For filling and emptying the treatment tank **40** with the different treatment liquids, a stub **47** which is brought through the bottom of the heating tank **44**, is attached at its lowest point. For sealing, the bottom of the heating tank **44** is clamped between a shoulder **48** and an intermediate flange **49**; the connecting flange **50** of a three-way valve **51** is bolted to the intermediate flange **49** at the same time. The two free connecting flanges **52** and **53** of the three-way valve **51** are provided for filling and emptying an electrolyte or different rinsing liquids.

An electroplating drum **54** which consists of two circular end walls **55** and **56** and a perforated drum case **57** of hexagonal cross section is disposed inside the treatment tank **40**. For inserting and removing the articles to be plated, one side surface of the drum case **57** can be taken off. This is not shown in detail in the drawing, however. The plating drum **54** must be made of electrically insulating materials so that the electroplating process is not disturbed. Suitable materials are, for instance, phenolic plastic laminates with paper as the resin carrier. The end wall **55** is connected to a miter gear **58** which is rotatably supported on a journal **59**, while the end wall **56** is rotatably supported in a bushing **60**. The plating drum **54** is mounted inside the treatment tank **40** on support arms **61** and **62** which are rigidly connected to the cover **42** via the journal **59** and the bushing **60**. The plating drum **54** is driven by a miter gear **63** meshing with the miter gear **58**; its drive shaft **64** is brought through the cover **42** and is coupled to the drive shaft **65** of a motor **66** which is taken off vertically

downward. The feed-through of the drive shaft **64** through the cover **42** is sealed by a stuffing gland **67**, while the motor **66** is fastened to the cover **42** via a bracket **68**. The miter gears **58** and **63** are covered by a cap **69** for protection against undesired deposition of aluminum.

The current is brought to the articles to be plated via a cathode terminal **70** and an insulated conductor **71**, which is brought into the plating drum **54** through the inclined hole of an insert **72** of the bushing **60** and ends in a contact element **73**. The feedthrough of the conductor **71** through the cover **42** is sealed. An anode **74**, which is arranged in a circular arc at a distance from the plating drum **54** is bolted by means of supports welded to its end faces, to angles **77** and **78**. These angles **77** and **78** are fastened to the cover **42** via an insulating spacer **79** and an insulating bushing **80**. An anode lead **81** is connected to the angle **78** in a conducting manner through the insulating bushing **80**.

Vapors rising from the treatment tank **40** are conducted into a reflux cooler **82**, which has inlet stub **83** connected to the upper cover plate **41** of the treatment tank **40**. The vapors are condensed at the cooling coil **84** of the reflux cooler **82**, the condensate returning through the inlet stub **83** to the treatment tank **40**. At the jacket of the reflux cooler **82**, two connections are provided. The lower connection **86** is provided for feeding in a protective gas and the upper connection **86** for the discharge of excess protective gas and for the pressure relief of the treatment tank **40**.

The apparatus described in the foregoing specification is particularly well suited for the batchwise aluminizing of small parts in mass production such as screws, nuts, washers and the like. The operation of the apparatus can be automated to a large degree.

We claim:

1. Apparatus for electrodepositing aluminum from aprotic, oxygen-free and water-free organo-aluminum electrolytes, comprising:

a. a heated treatment tank;

b. means to close said tank airtight;

c. means to admit an inert gas to said tank;

d. a rotatable electroplating drum arranged within said treatment tank;

e. a first tank for storing the electrolyte connected through a first valve and first pumping means to the treatment tank; and

f. a second tank for storing a rinsing liquid connected through a second valve and second pumping means to the treatment tank, whereby electrolyte and rinsing liquid may be transferred to and from said treatment tank by operation of said valves and pumping means.

2. Apparatus according to claim **1**, and further including means to heat said first tank.

3. Apparatus according to claim **1** and further including a third tank for storing a second rinsing liquid connected to said treatment tank.

4. Apparatus according to claim **2** and further including feed pumps connecting said treatment tank to said first and second tanks.

5. Apparatus according to claim **1** wherein said means to close said treatment tank comprises a cover to which said electroplating drum is fastened.

6. Apparatus according to claim **1** and further including a reflux cooler in the upper portion of said treatment tank.

7. Apparatus according to claim **1** and further including a relief line the end of which is immersed in an inert sealing liquid connected to said treatment tank.

8. A method for electrodepositing aluminum from aprotic, oxygen-free and water-free organo-aluminum electrolytes comprising:

a. placing a water-free inert aprotic rinsing liquid in a treatment tank under an inert gas;

b. subsequently removing said rinsing liquid to a holding tank;

c. then placing the electrolyte in the treatment tank;

d. electroplating; and

e. transferring said electrolyte into a storage tank.

9. The method according to claim **8** and further including immersing an electroplating drum with the articles to be plated in the treatment tank when it is filled with said rinsing liquid.

10. The method according to claim **8** and further including the step of filling the treatment tank with a second water-free inert aprotic rinsing liquid after the electrolyte is transferred.

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